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AUTHOR(S):

NORIMOTO, Misato; YAMADA, Tadashi

CITATION:

NORIMOTO, Misato ...[et al]. The Dielectric Properties of Wood VI : On the Dielectric Properties of the Chemical Constituents of Wood and the Dielectric Anisotropy of Wood. Wood research : bulletin of the Wood Research Institute Kyoto University 1972, 52: 31-43

ISSUE DATE:

1972-01-31

URL:

<http://hdl.handle.net/2433/53414>

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The Dielectric Properties of Wood VI*

On the Dielectric Properties of the Chemical Constituents of Wood and the Dielectric Anisotropy of Wood

Misato NORIMOTO** and Tadashi YAMADA**

Abstract—In this paper, the dielectric properties of the chemical constituents of wood were measured over a wide temperature and frequency ranges in order to elucidate the dielectric anisotropy of wood. In the case of cellulose and mannan the only one temperature dispersion was observed. The dispersion would be due to the rotational motions of methylol groups in the amorphous regions since the dispersion did not occur in xylan. On the other hand, the two dispersions were observed in lignin. The dispersion in high temperature range would be due to the motions of carbonyl groups to which water molecules are attached by hydrogen bonds, while the one in low temperature range would be due to the motions of methylol groups. The temperatures corresponding to the maximum dielectric loss factor for wood in the longitudinal direction coincided with that of cellulose and they were in higher range than those for wood in the transverse directions. These facts, therefore, show that the dielectric relaxation processes of wood in the longitudinal direction are governed by those of cellulose, while the relaxation processes of wood in the transverse directions are considerably influenced by those of lignin.

I. Introduction

It is well known that there exist variations in the magnitudes of dielectric constant of wood in the three principal directions, and that the magnitude of dielectric constant decreases generally in the order, longitudinal, radial, and tangential directions. Although many arguments on the dielectric anisotropy of wood have been presented, there are many problems remaining unsolved. Especially, the reports which discussed the dielectric anisotropy in connection with the relaxation processes have apparently not been published.

In the previous paper¹⁾, it was reported that the dielectric anisotropy of wood in the longitudinal and transverse directions is closely related to different modes of dipolar motions in both directions since the distribution for relaxation times in the longitudinal direction differs very much from that in the transverse directions. The present paper deals with the effect of grain angles in the three principal planes on the dielectric properties of wood and the dielectric properties of the chemical constituents of wood in order to elucidate the dielectric anisotropy of wood in

* Previous Paper, Wood Research, No. 51, 12 (1971).

** Division of Wood Physics.

more detail.

II. Experimental

Wood (HOONOKI, HINOKI and Lawson Cypress) and the chemical constituents of wood (cellulose, mannan, xylan, and lignin) were used as samples. The characteristics of the samples are shown in Table 1. The measurements at oven-dried condition and low moisture content were performed over phosphorus pentoxide and silica gel, respectively. The instruments and the methods of measurement were all the same to the ones already referred to in the previous papers^{2,3)}. The sample disks of the chemical constituents of wood were pressed to 20 mm diameter and about 1 mm thickness under the pressure. The measurements of dielectric constant and of loss factor were made over the frequency range from 300 Hz to 9.4 GHz and over the temperature range from -70 to 80°C .

Table 1. The characteristics of the samples.

Specimen	Specific gravity	Moisture content (%)	Direction
HOONOKI (<i>Magnolia obovata</i> THUNB.)	0.51	11.3	Three principal planes
HINOKI (<i>Chamaecyparis obtusa</i> ENDL.)	—	0	Three principal planes
Lawson Cypress (<i>Cupressus lawsoniana</i> MURR.)	0.39	8.2	LR plane
Cellulose (Merk)	1.25 1.19	0	—
Mannan (devil's tongue)	1.28	0	—
Beech xylan	1.26	0	—
Beech MWL	1.21	0 0.84	—
Bamboo MWL	1.21	0 0.90	—

III. Results and Discussion

3-1. The effect of grain angle on the dielectric properties of wood

As mentioned in the introduction, in the three principal directions the magnitude of dielectric constant decreases generally in the order, longitudinal (L), radial (R), tangential (T) directions. KRÖNER et al.⁴⁾ and NAKATO⁵⁾ reported that the dielectric anisotropy is mainly caused by the macroscopic structures of wood, whereas SKAAR suggested that the anisotropy may be ascribed to the molecular structures of cell wall⁶⁾. In the previous paper¹⁾, it was reported that the dielectric anisotropy is caused only by the macroscopic structures in very high frequency region in which the deformation polarizations contribute to dielectric constant, while the anisotropy is caused by the molecular structures of wood substance as

well as the macroscopic structures of wood cell because the magnitude of dielectric constant in L-direction is greater than that in R- or T- direction. The grain angle dependences of the dielectric constant and loss factor of wood in LR, LT and RT planes are discussed in this section.

The report which deals with the effect of grain angle on the dielectric properties of wood has not hitherto been known. Figs. 1~4 show the effect of grain angle on dielectric constant $\epsilon'(\theta)$ and dielectric loss factor $\epsilon''(\theta)$ of air dried HOONOKI and over-dried HINOKI in the three principal planes at 10 kHz and

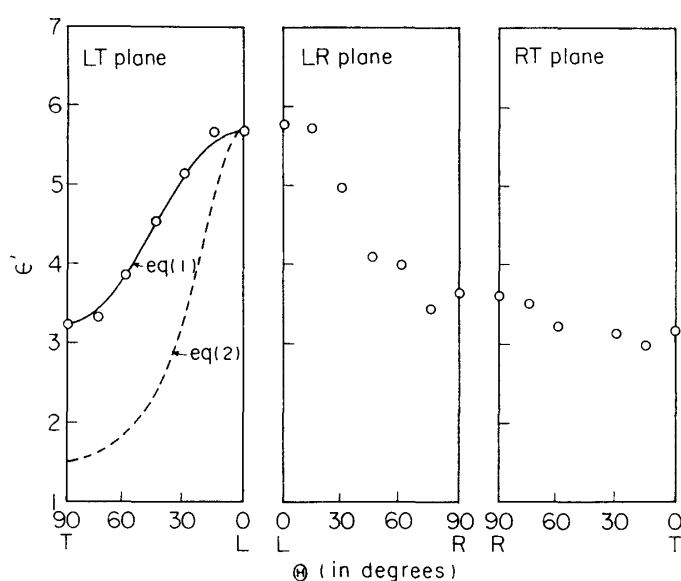


Fig. 1. The effect of grain angle on dielectric constant of HOONOKI. 23°C, 10 kHz, 11.3 %m.c.

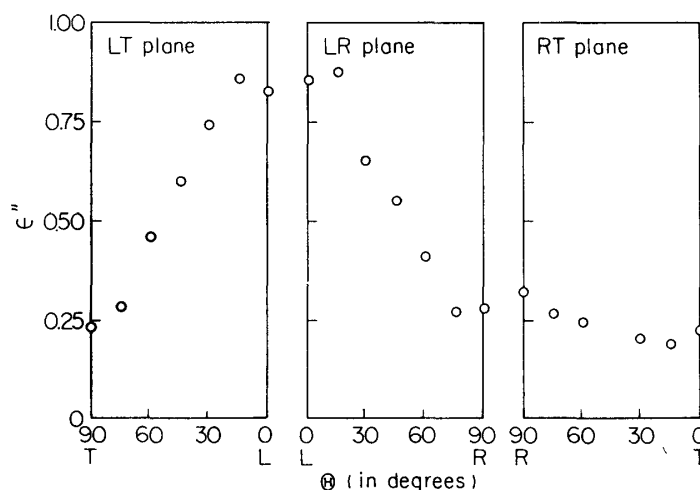


Fig. 2. The effect of grain angle on dielectric loss factor of HOONOKI. 23°C, 10 kHz, 11.3 %m.c.

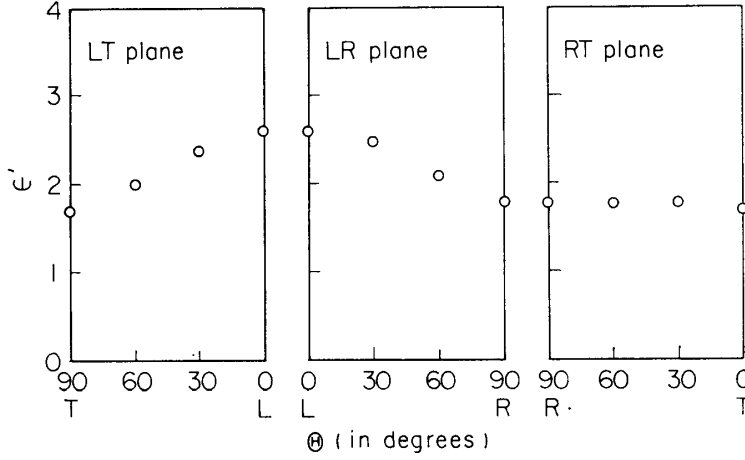


Fig. 3. The effect of grain angle on dielectric constant of HINOKI. 30°C, 10 kHz, 0 %m.c.

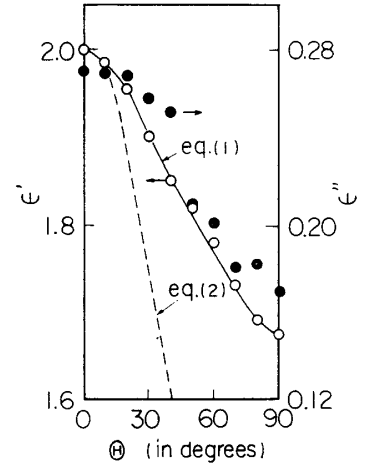


Fig. 4. Dielectric constant and dielectric loss factor of Lawson Cypress for grain angles in LR plane. 20°C, 9.4 GHz, 8.2 %m.c.

those of air-dried Lawson Cypress in LR plane at 9.4 GHz, respectively. The values of $\epsilon'(\theta)$ and $\epsilon''(\theta)$ for HONOKI in LR and LT planes at 10 kHz decreased with increasing grain angle except small grain angles, whereas those for Lawson Cypress at 9.4 GHz in LR plane decreased monotonously in magnitude as grain angle increased. In RT plane it seemed that $\epsilon'(\theta)$ and $\epsilon''(\theta)$ decreased slightly in magnitude with decreasing grain angle.

The following empirical equation held for $\epsilon'(\theta)$ in LR and LT planes.

$$\epsilon'(\theta) = \left(\epsilon'(0) - \epsilon'\left(\frac{\pi}{2}\right) \right) \cos 2\theta + \epsilon'\left(\frac{\pi}{2}\right), \quad (1)$$

$$0 \leq \theta \leq \frac{\pi}{2},$$

where $\epsilon'(0)$ is the dielectric constant in L-direction and $\epsilon'(\pi/2)$ is that in R- or T-direction. The solid lines in Figs. 1 and 4 represent the curves calculated from the empirical equations. The curves agreed well with the empirical values, especially with values at very high frequency.

On the other hand, the theoretical equation for $\epsilon'(\theta)$ in LR and LT planes can be obtained by applying the theory⁷⁾ on the dielectric constant for lamellar mixture consisting of two kinds of dielectrics to wood.

$$\epsilon'(\theta) = \frac{(\alpha+1)\epsilon_1'}{\epsilon_1' \cos^2 \theta + (\epsilon_1' - \alpha)(\alpha+1) \sin^2 \theta}, \quad (2)$$

$$\alpha = \frac{\gamma}{\gamma_1}(\epsilon_1' - 1),$$

where γ is the specific gravity, γ_1 the specific gravity of wood substance, and ϵ_1' the dielectric constant of wood substance. In the equation (2), it is assumed that the dielectric constants in the longitudinal and transverse directions can be represented by WIENER's equations.

The broken lines in Figs. 1 and 4 represent the theoretical curves calculated by the equation (2). Although the calculated curves did not agree well with the experimental values, the curves showed qualitatively that the value of $\epsilon'(\theta)$ decreases with increasing grain angle even in the region of small grain angle. As mentioned above, in the low frequency region in which only the orientation polarization contributes to loss factor, $\epsilon''(\theta)$ versus θ curve had a maximum in the region of small grain angle, while in very high frequency region in which the deformation polarization contributes mainly to dielectric constant the values of $\epsilon'(\theta)$ decreased monotonously with increasing grain angle. These facts show that the dielectric anisotropy of wood substance would be caused by the orientation polarization due to the rotational motions of the dipoles, and that the magnitude of dielectric constant of wood substance takes its maximum value at the small grain angle.

Figs. 5 and 6 show ϵ' versus frequency curves and ϵ' versus temperature curves for oven-dried HOONOKI at the three different grain angles in LT plane,

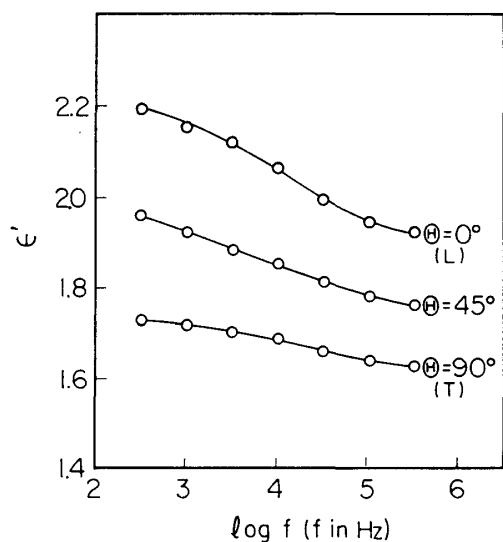


Fig. 5. Dielectric constant of oven-dried HOONOKI for three grain angles in LT plane as a function of frequency at -70°C .

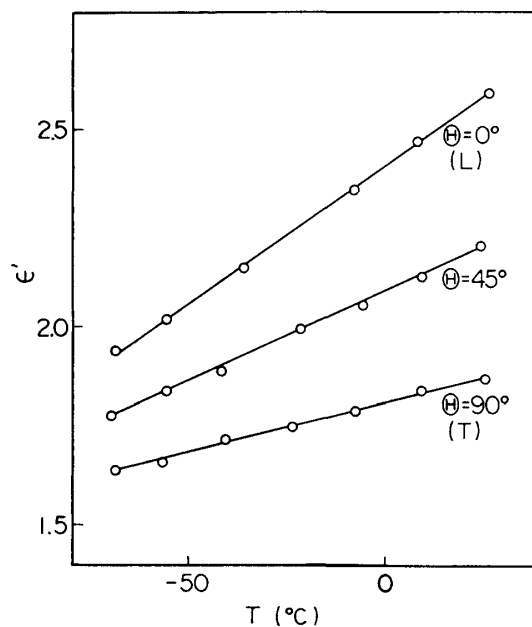


Fig. 6. Dielectric constant of oven-dried HOONOKI for three grain angles in LT plane as a function of temperature at 100 kHz.

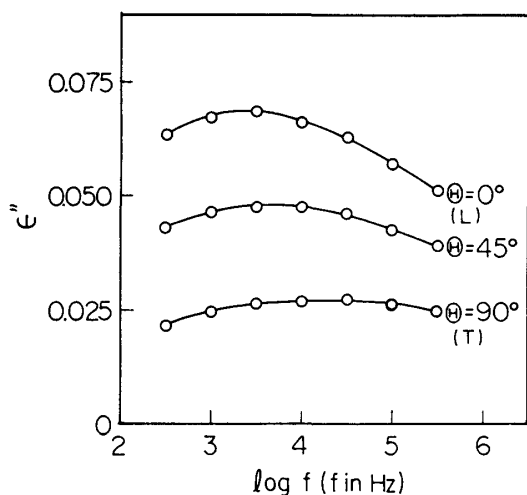


Fig. 7. Dielectric loss factor of oven-dried HOONOKI for three grain angles in LT plane as a function of frequency at -70°C .

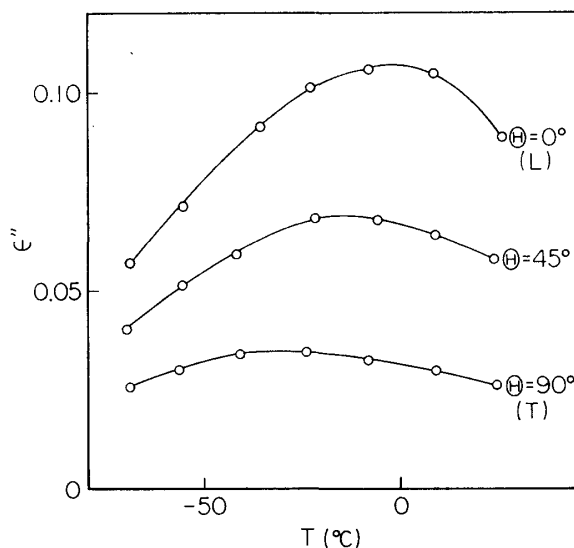


Fig. 8. Dielectric loss factor of oven-dried HOONOKI for three grain angles in LT plane as a function of temperature at 100 kHz.

respectively. ϵ' decreased in magnitude with increasing frequency and with decreasing temperature. Figs. 7 and 8 show ϵ'' versus frequency curves and ϵ'' versus temperature curves for oven-dried HOONOKI at the three different grain angles in LT plane, respectively. The frequency and temperature corresponding to ϵ'' maximum shifted to higher frequency and lower temperature ranges with increasing grain angle, respectively. From these results, it is evident that the dielectric anisotropy of wood depends on the macroscopic structures of wood as well as the relaxation process of dipoles.

3-2. The dielectric properties of the chemical constituents of wood

The dielectric properties of the chemical constituents of wood are discussed in this section in order to explain the anisotropy of the dielectric relaxation process of wood in the longitudinal and transverse directions. Many reports on the dielectric properties of cellulose have been presented. However, there is no report on the dielectric properties of the hemicelluloses and lignin.

Fig. 9 shows the results of ϵ'' as a function of temperature at several frequencies for dry cellulose. The only one absorption was observed within the frequency and temperature ranges studied. The temperature corresponding to the loss maximum f_m shifted to lower temperature region and the value of f_m decreased with decreasing frequency. Fig. 10 shows the results of ϵ'' as a function of frequency at several temperatures for dry cellulose. The frequency corresponding to ϵ''_{max} shifted to lower frequency and the value of ϵ''_{max} decreased with

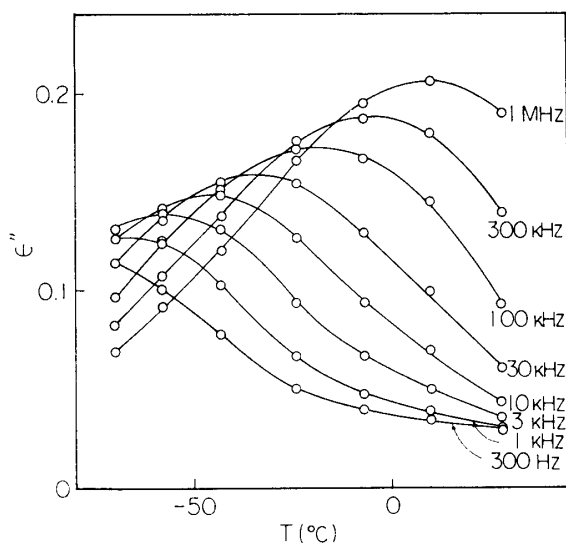


Fig. 9. Dielectric loss factor of cellulose as a function of temperature at respective frequencies.

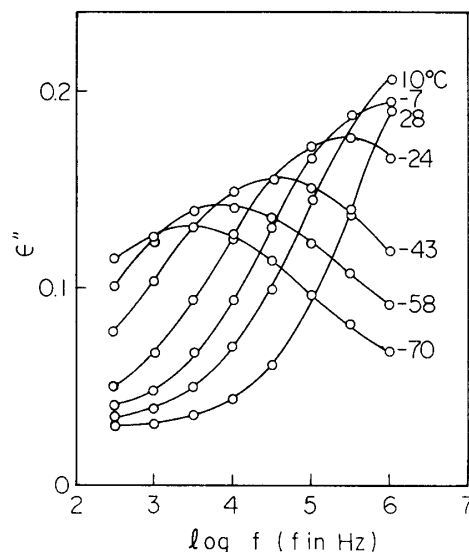


Fig. 10. Dielectric loss factor of cellulose as a function of frequency at respective temperatures.

decreasing temperature. In order to determine the energy of apparent activation ΔE , the logarithm of the frequency corresponding to loss maximum $\log f_m$ was plotted against the reciprocal of absolute temperature $1/T$. The $\log f_m - 1/T$ plots for cellulose gave the straight line and the value of ΔE calculated from the slope of this line was about 10 kcal/mole.

The existence of the dielectric absorption in cellulose has been shown by many authors⁸⁻¹⁰. ISHIDA et al.⁹) measured the dielectric properties of the three cellulose fibers and reported that the dipoles in the amorphous region and on the surface of the crystallite provide the chief contribution to this dispersion since the order of the magnitude of $(\epsilon_0' - \epsilon_\infty')$ for the samples parallels that of the accessibility of the samples. MIKHAILOV et al.¹⁰) investigated the dielectric relaxations of cellulose and its derivatives and suggested that the dispersion may be due to the movement of methylol groups in the less ordered zones of the polymers. Fig. 11 shows the results of ϵ'' as a function of temperature at various frequencies for dry mannan. The loss peaks at respective frequencies for mannan were almost identical in the location with those of cellulose. Hence, there was no great difference between the values of the activation energy for cellulose and mannan. Fig. 12 shows the results of ϵ'' as a function of frequency at several temperatures for dry mannan. Fig. 13 shows ϵ'' versus temperature curves at respective frequencies for dry beech xylan and Fig. 14 shows ϵ'' versus frequency curves at respective temperatures for dry beech xylan. The behaviors of ϵ'' for xylan differed very much from those for cellulose and mannan. The absorption occurred in cellulose and mannan

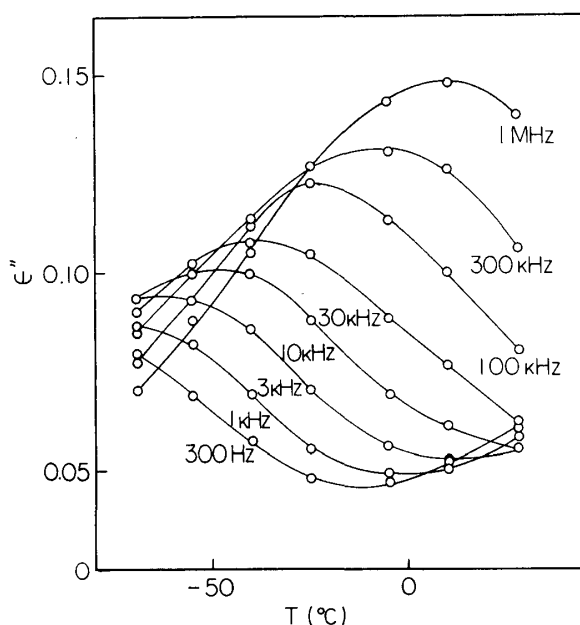


Fig. 11. Dielectric loss factor of mannan as a function of temperature at respective frequencies.

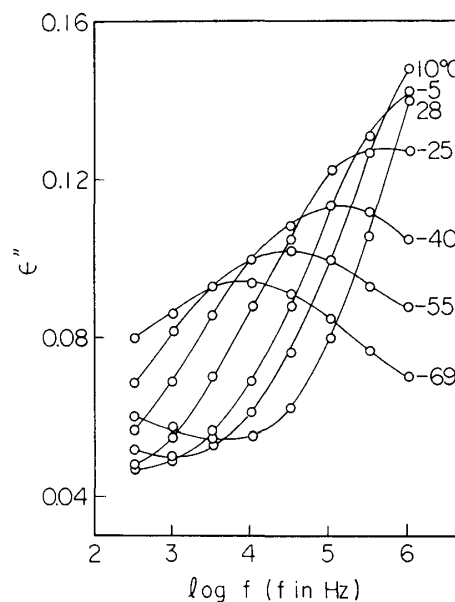


Fig. 12. Dielectric loss factor of mannan as a function of frequency at respective temperatures.

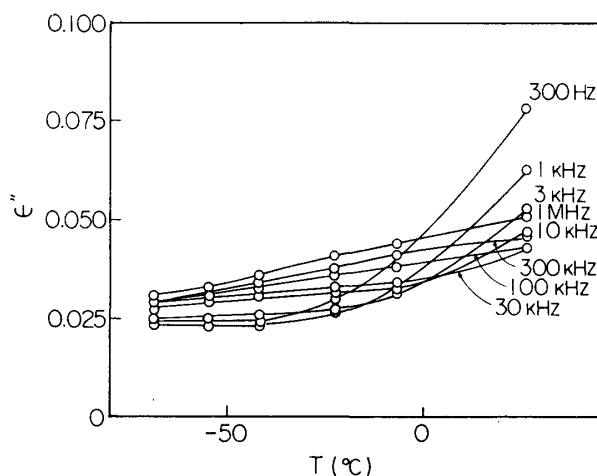


Fig. 13. Dielectric loss factor of beech xylan as a function of temperature at respective frequencies.

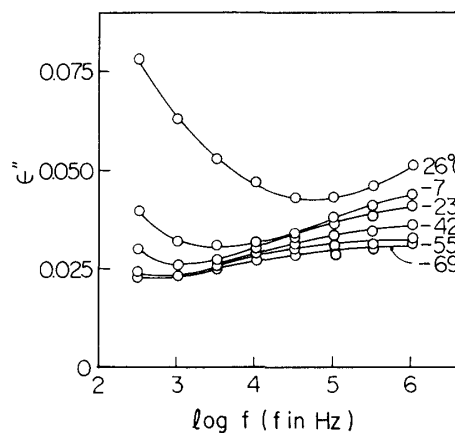


Fig. 14. Dielectric loss factor of beech xylan as a function of frequency at respective temperatures.

did not occur in xylan. It seems, therefore, that the relaxation process appeared in cellulose and mannan would be due to the rotational motions of methylol groups. Figs. 15 and 16 show ϵ'' versus temperature curves at various frequencies for dry milled wood lignin (MWL) and for MWL containing small amount of water, respectively. As is evident from the figures, the two absorptions were observed, although the magnitude of ϵ'' was very small compared with those of cellulose

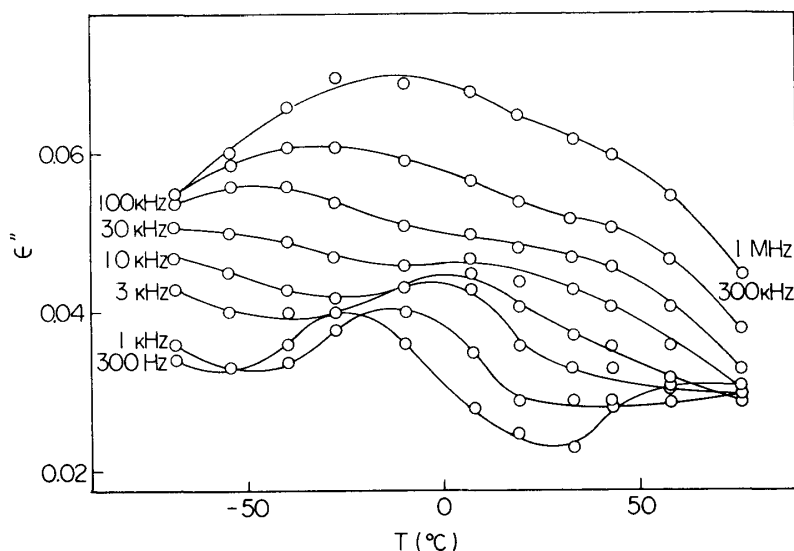


Fig. 15. Dielectric loss factor of beech MWL as a function of temperature at respective frequencies.

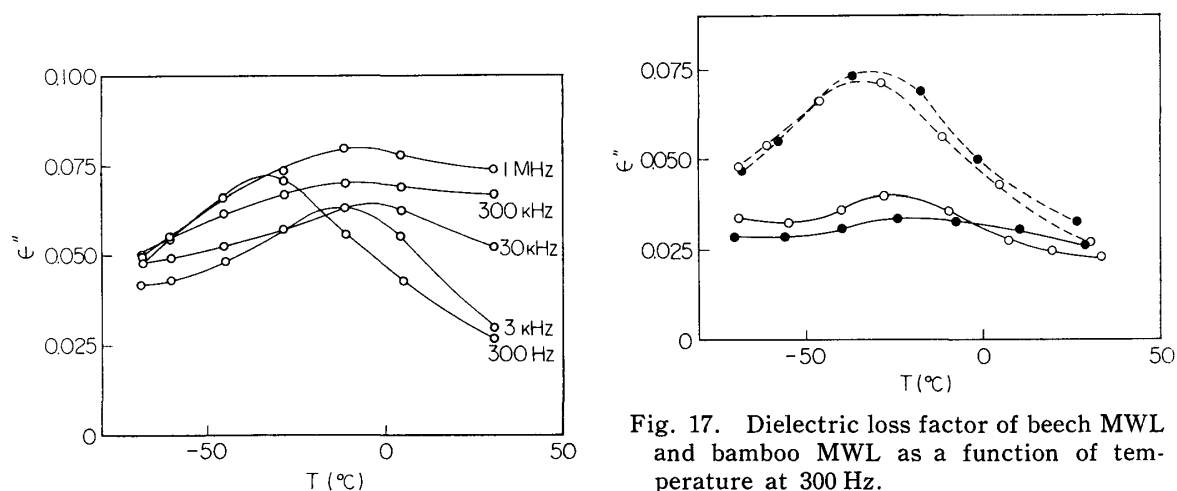


Fig. 16. Dielectric loss factor of beech MWL as a function of temperature at respective frequencies. 0.84 %m.c.

Fig. 17. Dielectric loss factor of beech MWL and bamboo MWL as a function of temperature at 300 Hz.

- beech MWL, 0 %m.c.
- bamboo MWL, 0 %m.c.
- beech MWL, 0.84 %m.c.
- bamboo MWL, 0.90 %m.c.

and mannan. For convenience, the absorptions are called the low temperature absorption and the high temperature one, respectively. The magnitude of the low temperature absorption was greater than that of the high temperature one. When the results of Fig. 15 is compared with those in Fig. 16, it is evident that the high temperature absorption increases in magnitude by adsorption of small amount of water, whereas the low temperature absorption is not influenced remarkably by adsorption of small amount of water. In Fig. 17 ϵ'' for beech and bamboo MWLs as a function of temperature at 300 Hz is shown. As is shown in the figure, it is

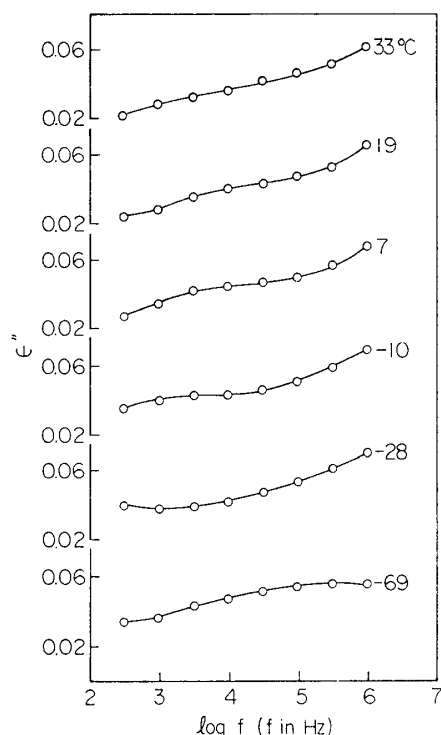


Fig. 18. Dielectric loss factor of beech MWL as a function of frequency at respective temperatures. 0 %m.c.

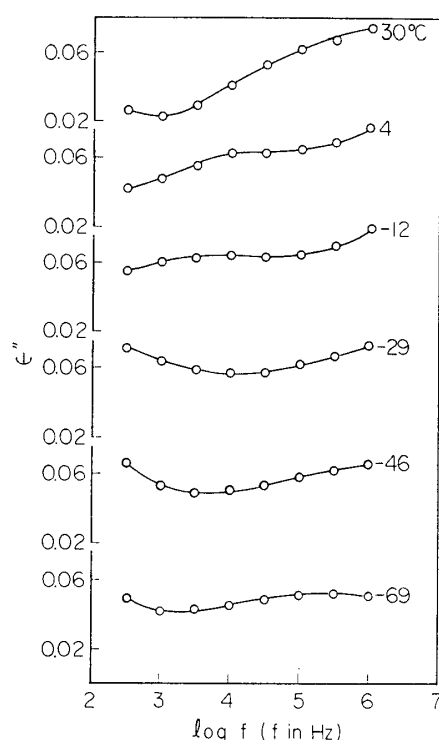


Fig. 19. Dielectric loss factor of beech MWL as a function of frequency at respective temperatures. 0.84 %m.c.

evident that the high temperature absorption is influenced remarkably by adsorption of small amount of water. Figs. 18 and 19 show ϵ'' as a function of frequency for beech MWL at 0% and 0.84% moisture content, respectively. Figs. 20 and 21 show those for bamboo MWL at 0% and 0.90% moisture content, respectively. The two frequency absorptions were observed and for convenience the absorptions are called the high frequency absorption and the low frequency one, respectively. The two loss peaks shifted to lower frequency region with decreasing temperature and the magnitude of the absorptions decreased with decreasing temperature. The low frequency absorption increased remarkably in magnitude by adsorption of small amount of water, while the high frequency one was not influenced by it. In the case of lignin it seems that the motions of the dipoles such as OH, OCH₃, CO and CH₂OH groups are dielectrically active. However, since it is reported that from the results of the dielectric measurements for metylcellulose and cellulose triacetate the relaxation processes due to the motions of OH and OCH₃ groups do not occur within the frequency and temperature ranges studied¹⁰⁾, the motions of two dipoles, CO and CH₂OH groups, can contribute eventually to dielectric loss. Furthermore, the measurement of the dielectric properties of nylon and polyethylene terephthalate¹¹⁾ showed that CO groups can only contribute to

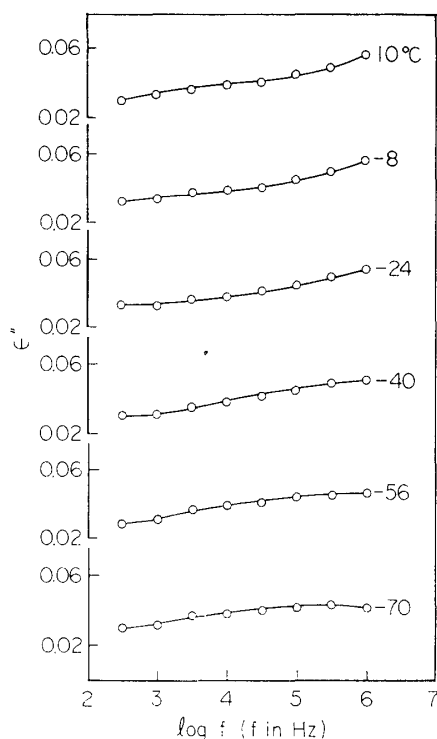


Fig. 20. Dielectric loss factor of bamboo MWL as a function of frequency at respective temperatures. 0 %m.c.

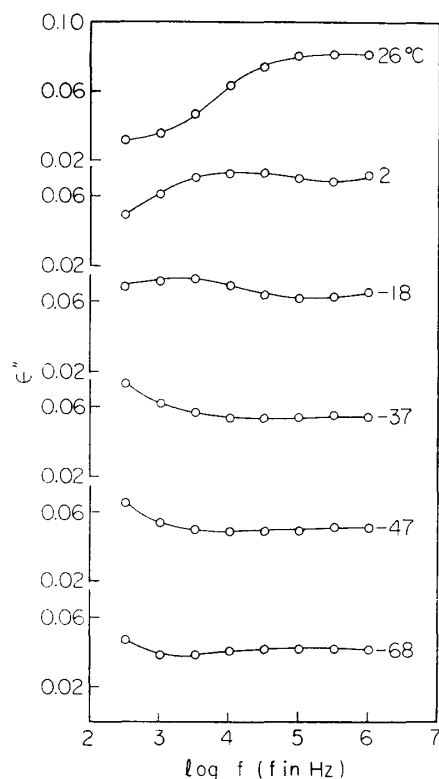


Fig. 21. Dielectric loss factor of bamboo MWL as a function of frequency at respective temperatures. 0.90 %m.c.

dielectric loss by the adsorption of water, and therefore this dielectric loss is due to the motion of CO groups to which water molecules are attached by hydrogen bonds. The high temperature absorption in lignin would be due to the motions of CO-H₂O complexes, since this relaxation process has same characters as that of nylon and polyethylene terephthalate. Hence, it may be concluded that the high temperature absorption is attributed to the motion of CH₂OH groups. As the absorption due to CH₂OH groups of lignin occurs in lower temperature region compared with that of cellulose and mannan, CH₂OH groups in lignin is more mobile than that in cellulose and mannan.

Fig. 22 shows ϵ'' as a function of frequency for HOONOKI in three principal directions, cellulose, and beech MWL at -58°C. As is evident from the figure, the anisotropy in the relaxation process could not be observed in the transverse directions. The frequency corresponding to the loss peak f_m for HOONOKI in L-direction coincided with that of cellulose and that it was in lower frequency range than those in R- and T-directions by one decade. Therefore, it seems that the dielectric properties of wood in the transverse directions are considerably influenced by those of lignin, since f_m for MWL was in higher frequency region than that

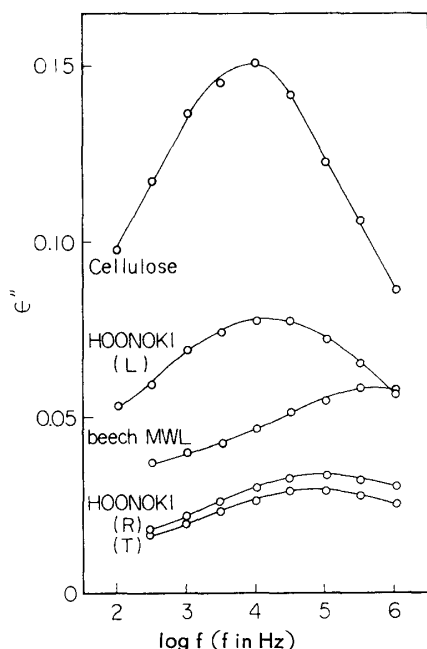


Fig. 22. Dielectric loss factor vs. frequency curves for HOONOKI, cellulose and beech MWL at -58°C .

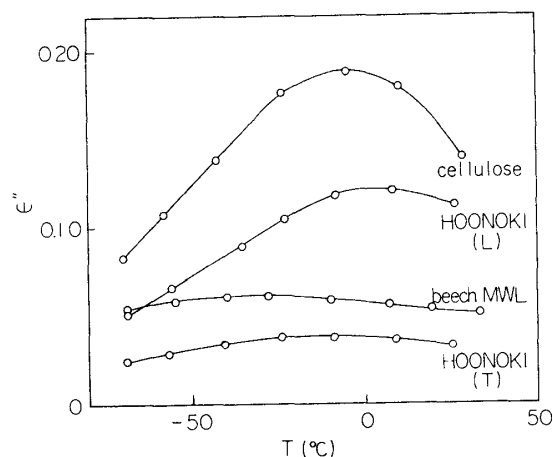


Fig. 23. Dielectric loss factor of HOONOKI, cellulose and beech MWL as a function of temperature at 300 kHz.

of cellulose. Fig. 23 shows ϵ'' as a function of temperature for HOONOKI in T- and L-directions, cellulose, and beech MWL at 300 kHz. The behavior of ϵ'' for HOONOKI in L-direction was similar to that of cellulose, whereas the behavior of ϵ'' for HOONOKI in T-direction was considerably influenced by that of lignin.

From the results in sections 3-1 and 3-2, it may be concluded that the dielectric properties of wood are governed by those of cellulose and mannan in the longitudinal direction and are considerably influenced by those of lignin in the transverse directions. Furthermore, it may be concluded that there are two stable orientational positions along the directions of microfibrils for each CH_2OH dipole of cellulose in the disordered region.

Acknowledgement

The authors wish to thank Prof. T. HIGUCHI, Dr. A. SATO, and Mr. E. MAEKAWA of our institute for their helpful advice and for supplying the samples.

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